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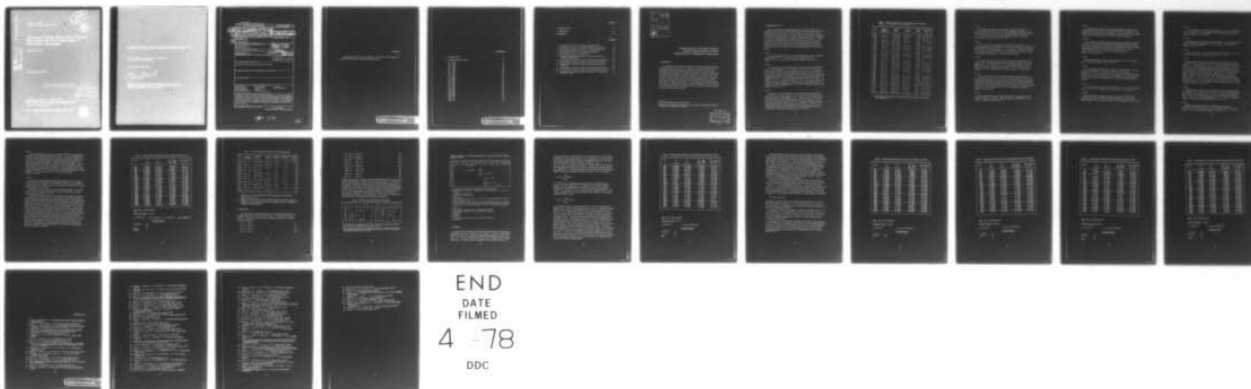
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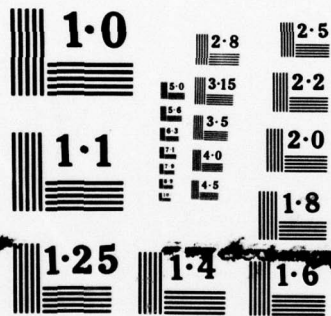
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Thermochemical and Kinetic Data of Gaseous Metal Oxides and Their Relationship to Atmospheric Composition

EDMOND MURAD

26 October 1977

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AERONOMY DIVISION PROJECT 6690
AIR FORCE GEOPHYSICS LABORATORY
HANSON AFB, MASSACHUSETTS 01931

AIR FORCE SYSTEMS COMMAND, USAF



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Dissociation energies	Ionization potentials														
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<p>The dissociation energies and ionization potentials of gaseous monoxides and dioxides of some metals are surveyed, and best values for these quantities are given. In addition, a survey is made of the kinetic data for the formation and destruction of these species and the results are tabulated. The relationship of these quantities to atmospheric composition is discussed, and it is shown that monoxide ions are converted to metal ions very quickly by reaction with atomic oxygen.</p>															

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Preface

I would like to thank Drs. K. S. Champion, R. S. Narcisi, and W. Swider for helpful discussions about atmospheric data and models.

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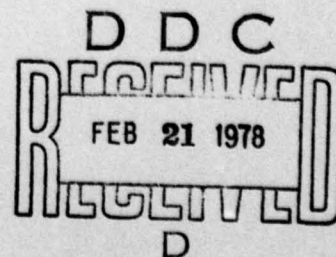
Thermochemical and Kinetic Data of Gaseous Metal Oxides and Their Relationship to Atmospheric Composition

1. INTRODUCTION

Thermochemical data (heats of formation or dissociation energies and ionization potentials) and kinetic data (rate constants for formation and destruction) for some metal oxides are needed because these metal oxides occur in the upper atmosphere either naturally or are released artificially, and may thus contribute to the chemical equilibrium in the upper atmosphere. In a previous report,¹ the reasons for interest in these oxides were discussed in some detail. This report presents a discussion of the current status of the thermochemical data and the kinetic data for selected metal oxides. At the conclusion, some comments will be made on the relation of this information to recent atmospheric studies. The choice of a particular metal oxide is somewhat arbitrary, but an effort has been made not to be too restrictive in this selection.

(Received for publication 25 October 1977)

Due to the large number of references (93) in this report, the references will not be footnoted. See references, page 29.



2. THERMOCHEMICAL DATA

Before discussing the individual molecules, it is in order to refer to two publications which discuss the dissociation energies of all the oxides in light of the information available at the time. One is by Drowart and Goldfinger,² and the other by Brewer and Rosenblatt.³ In addition, there is a more limited compilation of the dissociation energies of the rare-earth monoxides by Krause, Jr.⁴ Where no later data is available, these compilations will be used as sources. Table 1 presents the recommended values for the dissociation energies and ionization potentials of some metal oxides. Below is a discussion of the current status of each metal oxide. The monoxides are discussed alphabetically according to the metal.

2.1 AlO

The thermochemistry of AlO is fairly well established from several independent measurements.^{5, 6, 7} An analysis of all the data⁸ indicates that $D_O^0(\text{AlO}) = 121.4 \pm 1 \text{ kcal/mol}$ ($5.26 \pm 0.04 \text{ eV}$). $IP(\text{AlO}) = 9.53 \pm 0.15 \text{ eV}$.⁵

2.2 BaO

As in the case of AlO, the thermochemistry of BaO is quite well established now. A value of $D_O^0(\text{BaO}) = 131.0 \pm 2 \text{ kcal/mol}$ ($5.68 \pm 0.09 \text{ eV}$) is given in the JANAF tables⁹ and is based on data available up to June 1974. This value seems to be the best estimate at present, although higher values have been reported. An electron impact study¹⁰ yielded $D_O^0(\text{BaO}) = 132 \pm 5 \text{ kcal/mol}$, while a recent chemiluminescence study¹¹ and a laser-induced fluorescence study¹² have yielded $D_O^0(\text{BaO}) \geq 133.6 \pm 3.5 \text{ kcal/mol}$ and $D_O^0(\text{BaO}) = 133.5 \pm 1.3 \text{ kcal/mol}$, respectively. It may be necessary, eventually, to revise the JANAF value slightly upwards. A recent flame study¹³ yielded $D_O^0(\text{BaO}) = 5.30 \pm 0.10 \text{ eV}$, but this is surely too low. $IP(\text{BaO}) = 6.85 \pm 0.10 \text{ eV}$.¹⁴

2.3 CaO

An analysis of the data up to 1974 is given in the JANAF tables¹⁵ and that analysis has led to a value of $D_O^0(\text{CaO}) = 91 \pm 5 \text{ kcal/mol}$. A recent thermochemical measurement¹⁶ yielded $D_O^0(\text{CaO}) = 91.4 \pm 2 \text{ kcal/mol}$, while a recent chemiluminescence experiment¹¹ yielded $D_O^0(\text{CaO}) \geq 109.7 \pm 3.5 \text{ kcal/mol}$. Flame experiments have yielded $D_O^0(\text{CaO}) = 86.5 \pm 4.6 \text{ kcal/mol}$.¹³ It seems clear that the chemiluminescence experiments and the flame studies are in error. The JANAF value is preferred, and $D_O^0(\text{CaO}) = 91 \pm 5 \text{ kcal/mol}$ ($3.95 \pm 0.22 \text{ eV}$) is recommended. $IP(\text{CaO})$ has been reported to be $6.5 \pm 1 \text{ eV}$.¹⁷

Table 1. Thermochemical Data for the Gaseous Metal Monoxides.
 $D^{\circ}_O(O_2) = 117.97 \text{ kcal/mol } (5.12 \pm 0.0019 \text{ eV})$

MO	$D^{\circ}_O(\text{MO})$ kcal/mol	$D^{\circ}_O(\text{MO})$ eV	IP(MO) eV	IP(M) ^a eV	$D^{\circ}_O(\text{M}^+-\text{O})$ eV
AlO	121.4 ± 1	5.26 ± 0.04	9.53 ± 0.15	5.986	1.70 ± 0.15
BaO	131.0 ± 2	5.68 ± 0.09	6.85 ± 0.1	5.212	4.0 ± 0.1
CaO	91 ± 5	3.95 ± 0.2	6.5 ± 1	6.113	3.6 ± 1
CeO	188.3 ± 5	8.16 ± 0.22	4.90 ± 0.1	5.47	8.7 ± 0.3
CsO	[67 ± 6]	[2.9 ± 0.3]	---	3.894	---
EuO	111.9 ± 2.4	4.85 ± 0.10	6.3 ± 0.2	5.68	4.2 ± 0.2
FeO	96.8 ± 3	4.3 ± 0.13	8.71 ± 0.1	7.870	3.4 ± 0.15
GdO	169 ± 4	7.32 ± 0.17	5.75 ± 0.1	6.14	7.7 ± 0.2
KO	[65 ± 6]	[2.8 ± 0.3]	---	4.341	---
LaO	190.0 ± 3	8.24 ± 0.13	4.95 ± 0.19	5.577	8.9 ± 0.2
LiO	80.5 ± 1.5	3.49 ± 0.06	8.45 ± 0.2	5.392	0.43 ± 0.21
MgO	80 ± 6	3.46 ± 0.3	---	7.646	---
NaO	60.3 ± 4	2.61 ± 0.2	7.4 ± 0.4	5.139	~0.3
NdO	166 ± 3	7.20 ± 0.13	4.97 ± 0.1	5.49	7.7 ± 0.2
NiO	88 ± 3	3.82 ± 0.13	9.5 ± 0.3	7.635	2.0 ± 0.3
PbO	88.4 ± 2	3.83 ± 0.09	9.0 ± 0.3	7.416	2.3 ± 0.3
PrO	176.2 ± 3	7.64 ± 0.13	4.90 ± 0.1	5.42	8.2 ± 0.2
ScO	161.5 ± 3	7.00 ± 0.13	6.6 ± 0.3	6.54	6.9 ± 0.3
SeO	100 ± 15	4.3 ± 0.7	---	9.752	---
SiO	190.9 ± 2	8.28 ± 0.09	11.6 ± 0.2	8.151	4.8 ± 0.2
SmO	136.0 ± 2	5.90 ± 0.09	5.5 ± 0.1	5.63	6.0 ± 0.1
SnO	126.5 ± 2	5.49 ± 0.09	9.8 ± 0.5	7.344	3.0 ± 0.5
SrO	101 ± 4	4.38 ± 0.17	6.1 ± 1	5.695	4.0 ± 1
ThO	202.7 ± 3.2	8.79 ± 0.14	≥6.0 ± 0.1	6.2 ± 0.2 ≤9.0	±0.2
TiO	158.4 ± 2	6.87 ± 0.09	6.7 ± 0.1	6.82	7.0 ± 0.2
UO	181.2 ± 4	7.86 ± 0.17	5.72 ± 0.1	6.11	8.3 ± 0.2
YO	171.0 ± 3	7.41 ± 0.13	6 ± 1	6.38	7.8 ± 1
ZrO	181.9 ± 3.5	7.89 ± 0.15	6.0 ± 0.2	6.84	8.7 ± 0.2

a. Data taken from reference 65 except in the case of Th, where it was taken from reference 66.

2.4 CeO

The standard compilations referred to above give 190 ± 5 kcal/mol,⁴ 187 ± 6 kcal/mol,³ and 188.6 ± 3.5 kcal/mol² for $D_0^0(\text{CeO})$. However, in view of the work of Drowart et al¹⁸ who measured $D_0^0(\text{LaO}) - D_0^0(\text{CeO})$ and found it to be 1.7 ± 3.5 kcal/mol, a reasonable value of $D_0^0(\text{CeO})$, is 188.3 ± 5 kcal/mol (8.16 ± 0.22 eV). $\text{IP}(\text{CeO}) = 4.90 \pm 0.1$ eV.¹⁹

2.5 CsO

There are no reported measurements of $D_0^0(\text{CsO})$ nor for $\text{IP}(\text{CsO})$. Ionic model calculations have yielded $D_0^0(\text{CsO}) = 70 \pm 3$ kcal/mol²⁰ and 73 ± 6 kcal/mol.²¹ The JANAF tables²² estimate $D_0^0(\text{CsO}) = 62 \pm 10$ kcal/mol. Comparison with LiO and NaO suggests that perhaps the ionic model calculations are too high. A reasonable estimate is $D_0^0(\text{CsO}) = 67 \pm 6$ kcal/mol (2.90 ± 0.3 eV).

2.6 EuO

The dissociation energy of EuO has been the subject of considerable controversy recently. The chemiluminescence experiments have yielded a lower limit, $D_0^0(\text{EuO}) \geq 131.4 \pm 0.7$ kcal/mol.²³ It is clear now that this value is too high as shown by three later, independent investigations.^{24, 25, 26} The best value is $D_0^0(\text{EuO}) = 111.9 \pm 2.4$ kcal/mol (4.85 ± 0.10 eV). $\text{IP}(\text{EuO}) = 6.3 \pm 0.2$ eV.²⁴

2.7 FeO

There are two measurements of $D_0^0(\text{FeO})$ and these have yielded values of 97 ± 3 kcal/mol²⁷ and 96.8 ± 3 kcal/mol.²⁸ Recent spectroscopic studies on the ground state and low-lying states of FeO suggest a reordering and a reassignment of the states of FeO.²⁹ If these spectroscopic studies are confirmed, then it will be necessary to shift $D_0^0(\text{FeO})$ upwards by about 0.4 kcal/mol. For the time being, however, 96.8 ± 3 kcal/mol (4.20 ± 0.13 eV) is recommended for $D_0^0(\text{FeO})$. $\text{IP}(\text{FeO}) = 8.71 \pm 0.1$ eV.²⁸

2.8 GdO

Recent preliminary thermochemical experiments³⁰ were performed where $D_0^0(\text{GdO}) - D_0^0(\text{TiO})$ was measured. These experiments yield $D_0^0(\text{GdO}) = 169 \pm 4$ kcal/mol. $\text{IP}(\text{GdO}) = 5.75 \pm 0.10$ eV.¹⁹

2.9 KO

No measurements have been reported for either $D_o^o(\text{KO})$ or $\text{IP}(\text{KO})$. Ionic model calculations have yielded $71 \pm 6 \text{ kcal/mol}$ ²¹ and $71 \pm 3 \text{ kcal/mol}$.²⁰ Comparison with other alkali metal oxides suggests that these values may be too high. A value of $65 \pm 6 \text{ kcal/mol}$ ($2.8 \pm 0.3 \text{ eV}$) is recommended at this time.

2.10 LaO

Measurements of $D_o^o(\text{LaO})$ by independent investigators generally agree with each other. A recent chemiluminescence experiment which takes into account metastable excited states of the metal beam yielded $D_o^o(\text{LaO}) = 188.9 \pm 0.9 \text{ kcal/mol}$ in good agreement with the thermochemical measurements.³¹ A value of $190.0 \pm 3 \text{ kcal/mol}$ ($8.24 \pm 0.13 \text{ eV}$) is recommended for $D_o^o(\text{LaO})$. $\text{IP}(\text{LaO}) = 4.95 \pm 0.19 \text{ eV}$.¹⁴

2.11 LiO

Recent thermochemical measurements yield $D_o^o(\text{LiO}) = 80.5 \pm 1.5 \text{ kcal/mol}$ ($3.49 \pm 0.06 \text{ eV}$) and $\text{IP}(\text{LiO}) = 8.45 \pm 0.20 \text{ eV}$.³²

2.12 MgO

In a recent JANAF supplement,¹⁵ a value of $80 \pm 6 \text{ kcal/mol}$ ($3.5 \pm 0.3 \text{ eV}$) was chosen for $D_o^o(\text{MgO})$. A recent thermochemical study³³ yielded $D_o^o(\text{MgO}) = 85.7 \pm 0.5 \text{ kcal/mol}$, while a spectroscopic study of MgO spectra generated by shock-heating of MgO particles led to $D_o^o(\text{MgO}) = 93.2 \pm 8.4 \text{ kcal/mol}$.³⁴ Both of these results seem too high and for the time being the JANAF value is preferred.

2.13 NaO

A mass spectrometric measurement of $D_o^o(\text{NaO})$ gave a value of $60.3 \pm 4 \text{ kcal/mol}$ (or $2.61 \pm 0.2 \text{ eV}$).³⁵ $\text{IP}(\text{NaO})$ has been reported to be $\sim 7.4 \pm 0.4 \text{ eV}$.³²

2.14 NdO

Mass spectrometric measurements were recently performed³⁰ whereby $D_o^o(\text{NdO})$ was measured by reference to $D_o^o(\text{ScO})$ and $D_o^o(\text{TiO})$. These results indicate $D_o^o(\text{NdO}) = 166 \pm 3 \text{ kcal/mol}$ ($7.20 \pm 0.13 \text{ eV}$). $\text{IP}(\text{NdO}) = 4.97 \pm 0.1 \text{ eV}$.¹⁹

2.15 NiO

Two thermochemical studies have yielded $D_o^O(\text{NiO}) = 86.5 \pm 5 \text{ kcal/mol}^{36}$ and $89.3 \pm 3 \text{ kcal/mol}^{37}$. A value of $D_o^O(\text{NiO}) = 88 \pm 3 \text{ kcal/mol}$ ($3.82 \pm 0.09 \text{ eV}$) is selected. $\text{IP}(\text{NiO}) = 9.5 \pm 0.3 \text{ eV}^{36}$

2.16 PbO

The dissociation energy of PbO is well established. Two independent thermochemical studies^{38, 39} yield $D_o^O(\text{PbO}) = 88.4 \pm 2 \text{ kcal/mol}$ ($3.83 \pm 0.09 \text{ eV}$). $\text{IP}(\text{PbO}) = 9.0 \pm 0.2 \text{ eV}^{39, 40}$

2.17 PrO

Recent thermochemical measurements³⁰ have yielded $D_o^O(\text{PrO}) = 176.2 \pm 3 \text{ kcal/mol}$ ($7.64 \pm 0.13 \text{ eV}$). $\text{IP}(\text{PrO}) = 4.90 \pm 0.1 \text{ eV}^{19}$

2.18 ScO

The dissociation energy of ScO has been measured by reference to $D_o^O(\text{LaO})$ and $D_o^O(\text{YO})$.⁴¹ $D_o^O(\text{LaO})$ and $D_o^O(\text{YO})$ are discussed in their respective sections; it suffices to say here that $D_o^O(\text{LaO}) = 190.0 \pm 3 \text{ kcal/mol}$ and $D_o^O(\text{YO}) = 171.0 \pm 2 \text{ kcal/mol}$ are used. If free energy functions for ScO and YO are calculated using recent spectroscopic measurements⁴² and if the data of Smoes et al⁴¹ are recalculated using these functions, then $D_o^O(\text{YO}) - D_o^O(\text{ScO}) = 9.3 \pm 3 \text{ kcal/mol}$ and $D_o^O(\text{LaO}) - D_o^O(\text{ScO}) = 28.7 \pm 3 \text{ kcal/mol}$. These values lead to an average $D_o^O(\text{ScO}) = 161.5 \pm 3 \text{ kcal/mol}$ ($7.0 \pm 0.13 \text{ eV}$). The chemiluminescence experiments yield $D_o^O \geq 7.13 \pm 0.1 \text{ eV}$,⁴² but this seems to be too high. For reference, the thermochemical functions calculated with the new spectroscopic data are given in Table 2. $\text{IP}(\text{ScO}) = 6.6 \pm 0.3 \text{ eV}^{30}$

2.19 SeO

This dissociation energy is not well established. Spectroscopic studies indicated $D_o^O(\text{SeO}) = 100 \pm 15 \text{ kcal/mol}$ ($4.3 \pm 0.7 \text{ eV}$).³ There is no direct measurement of the ionization potential of SeO. However, the appearance potential for $\text{SeO}_2 + e \rightarrow \text{SeO}^+ + \text{O} + 2e$ has been reported to be $13.0 \pm 0.5 \text{ eV}$.^{43a} If $D_o^O(\text{SeO}-\text{O})$ is taken to be $\sim 100 \text{ kcal/mol}$,^{43b} then $\text{IP}(\text{SeO}) = 8.7 \pm 0.7 \text{ eV}$.

2.20 SiO

$D_o^O(\text{SiO})$ is well established and four independent thermochemical studies^{31, 44, 45, 46} agree fairly well. A value of $D_o^O(\text{SiO}) = 190.9 \pm 2 \text{ kcal/mol}$ ($8.28 \pm 0.09 \text{ eV}$) is recommended. $\text{IP}(\text{SiO}) = 11.6 \pm 0.2 \text{ eV}^{47}$

Table 2. Thermodynamic Functions of Gaseous Scandium Monoxide (ScO)

T (K)	C_p (E. U.)	S^0 (E. U.)	$H_T^0 - H_{298}^0$ (kcal/mol)	$-(G_T^0 - H_{298}^0)/T$ (E. U.)
300	7.38347	53.6831	.0136528	53.6377
400	7.75709	55.8593	.771095	53.9319
500	8.05541	57.6234	1.56245	54.4994
600	8.27354	59.1119	2.37948	55.1475
700	8.43137	60.3992	3.21515	55.8081
800	8.54727	61.5323	4.06437	56.4545
900	8.63433	62.5435	4.92365	57.0762
1000	8.70133	63.4561	5.79057	57.6697
1100	8.75414	64.2872	6.66344	58.2345
1200	8.79669	65.05	7.54105	58.7716
1300	8.83169	65.7547	8.42253	59.2825
1400	8.86106	66.4095	9.30721	59.7689
1500	8.88616	67.0209	10.1946	60.2328
1600	8.90804	67.5942	11.0843	60.6757
1700	8.92751	68.134	11.9761	61.0992
1800	8.94525	68.644	12.8698	61.5049
1900	8.96186	69.1272	13.7651	61.8941
2000	8.97787	69.5864	14.6621	62.2679
2100	8.99378	70.0239	15.5607	62.6275
2200	9.01006	70.4418	16.4609	62.974
2300	9.02715	70.8418	17.3627	63.308
2400	9.04547	71.2255	18.2664	63.6307
2500	9.06538	71.5943	19.1719	63.9425
2600	9.08722	71.9493	20.0795	64.2444
2700	9.11126	72.2918	20.9894	64.5368
2800	9.13776	72.6228	21.9018	64.8204
2900	9.16689	72.943	22.8171	65.0957
3000	9.19878	73.2534	23.7353	65.3632

$$H_{298}^0 - H_O^0 = 2.10011 \text{ kcal/mol}$$

Molecular Weight: 60.956

$$\omega_e = 975.7 \text{ cm}^{-1} \quad \omega_e x_e = 4.2 \text{ cm}^{-1} \quad \alpha = 0.0033 \text{ cm}^{-1} \quad \beta_e = 0.516$$

Electronic States

$\epsilon_i \text{ (cm}^{-1}\text{)}$	g_i
0	2
16849.3	2
16604.8	4

2.21 SmO

Recent mass spectrometric studies yield $D_O^O(\text{SmO}) = 136.0 \pm 2 \text{ kcal/mol}$ ($5.90 \pm 0.09 \text{ eV}$) and $IP(\text{SmO}) = 5.5 \pm 0.1 \text{ eV}$.⁴⁸

2.22 SnO

$D_O^O(\text{SnO})$ is well established from spectroscopic studies⁴⁹ and from thermochemical studies.⁵⁰ $D_O^O(\text{SnO}) = 126.5 \pm 2 \text{ kcal/mol}$ ($5.49 \pm 0.09 \text{ eV}$). $IP(\text{SnO}) = 9.8 \pm 0.5 \text{ eV}$.⁵⁰

2.23 SrO

The JANAF supplement⁹ gives a value of $D_O^O(\text{SrO}) = 101.0 \pm 4 \text{ kcal/mol}$ ($4.38 \pm 0.17 \text{ eV}$). Chemiluminescence experiments have yielded $D_O^O(\text{SrO}) \geq 107.7 \pm 3.5 \text{ kcal/mol}$,¹¹ but this value seems too high. Flame experiments¹³ have yielded $D_O^O(\text{SrO}) = 93.6 \pm 2.3 \text{ kcal/mol}$, but this value seems to be too low. At present, the JANAF value is preferred. $IP(\text{SrO}) = 6.1 \pm 1 \text{ eV}$.¹⁸

2.24 ThO

Three recent thermochemical measurements have yielded $D_O^O(\text{ThO}) = 207.5 \pm 2 \text{ kcal/mol}$,⁵¹ $202.7 \pm 3.2 \text{ kcal/mol}$,⁵² and $207.4 \pm 2.5 \text{ kcal/mol}$.⁵³ The differences are due in part to the use of different free energy functions. A value of $D_O^O(\text{ThO}) = 202.7 \pm 3.2 \text{ kcal/mol}$ ($8.79 \pm 0.14 \text{ eV}$) is recommended. $IP(\text{ThO}) \geq 6.0 \pm 0.1 \text{ eV}$.⁵²

2.25 TiO

Recent thermochemical measurements have yielded $D_O^O(\text{TiO}) = 158.2 \pm 3.7 \text{ kcal/mol}$ ⁵⁴ and $158.4 \pm 1.5 \text{ kcal/mol}$.⁵⁵ Chemiluminescence experiments in which corrections for metastable atom population in the metal beam were made yielded $D_O^O(\text{TiO}) = 159.8 \pm 3 \text{ kcal/mol}$.⁵⁶ These latter experiments seem a little high. The recommended value of $D_O^O(\text{TiO})$ is $158.4 \pm 2 \text{ kcal/mol}$ ($6.87 \pm 0.09 \text{ eV}$). $IP(\text{TiO}) = 6.70 \pm 0.10 \text{ eV}$.⁵⁵

2.26 UO

Thermochemical measurements by different investigators are in agreement and yield $D_O^O(\text{UO}) = 181.2 \pm 4 \text{ kcal/mol}$ ($7.86 \pm 0.17 \text{ eV}$).^{31, 57, 58} $IP(\text{U}) = 5.72 \pm 0.06 \text{ eV}$.⁵⁹

2.27 YO

Recent chemiluminescence studies on ScO and YO^{42, 60} have established the identities of low-lying energy states of YO and ScO. Free energy functions for YO were calculated using these new spectroscopic data and these functions were, in turn, used to recalculate $D_O^{\circ}(\text{LaO}) - D_O^{\circ}(\text{YO})$ from published results⁴¹ and $D_O^{\circ}(\text{YO})$ from vaporization studies.⁶¹ These studies now yield $D_O^{\circ}(\text{YO}) = 171.2 \pm 3$ kcal/mol and 170.7 ± 3 kcal/mol, respectively. The thermodynamic functions used in these calculations are given in Table 3. The chemiluminescence experiments⁴² yield $D_O^{\circ}(\text{YO}) \geq 173.0 \pm 2.3$ kcal/mol, this value seems too high. A value of $D_O^{\circ}(\text{YO}) = 171.0 \pm 3$ kcal/mol (7.41 ± 0.13 eV) is recommended. $\text{IP}(\text{YO}) = 6 \pm 1$ eV.⁶²

2.28 ZrO

Two thermochemical experiments have yielded $D_O^{\circ}(\text{ZrO}) = 180.7 \pm 2$ kcal/mol⁶³ and 181.9 ± 3.5 kcal/mol.⁶⁴ The difference is due to the use of different free energy functions. $D_O^{\circ}(\text{ZrO}) = 181.9 \pm 3.5$ kcal/mol (7.89 ± 0.15 eV) is recommended $\text{IP}(\text{ZrO}) = 6.0 \pm 0.2$ eV.⁶⁴

The results of the above discussion are summarized in Table 1. Also given in this table are the dissociation energies of the metal oxide ions, that is, the energy for the process $\text{MO}^+ \rightarrow \text{M}^+ + \text{O}$.

In addition to the monoxides there is some interest in the thermochemistry of the gaseous metal dioxides, but here the available data is quite sparse and often there is disagreement about the thermochemical observations. Compounding these problems is the fact that the electronic spectra and the vibrational frequencies for these dioxides are generally unknown, so that the free energy functions have sometimes to be conjured from intuitive feelings about spectral data. A case in point is that of gaseous AlO_2 which has been reported in a mass spectrometric study.⁶⁷ A study of the vaporization of $\text{Al}_2\text{O}_3(\text{s})$, however, has shown no evidence whatever for the formation of gaseous AlO_2 .⁶⁸ Thus at present, the thermochemical properties of $\text{AlO}_2(\text{g})$ should be considered questionable. Without further discussion, Table 4 shows the recommended values for the heats of atomization of some metal dioxides — namely, those for which there seems to be some reliable data. The dissociation energy $D_O^{\circ}(\text{MO}-\text{O})$, which is the energy required to break the first M-O bond, is obtained by subtracting $D_O^{\circ}(\text{MO})$ from the heat of atomization of the gaseous metal dioxide, $\Delta H_a(\text{MO}_2)$.

Table 3. Thermodynamic Functions of Gaseous Yttrium Monoxide (YO)

T (K)	C ^o (E. U.)	S ^o (E. U.)	H _T ^o - H ₂₉₈ ^o (kcal/mol)	-(G _T ^o - H ₂₉₈ ^o)/T (E. U.)
300	7.53214	55.9197	.0139269	55.8734
400	7.91869	58.1417	.78731	56.1738
500	8.19883	59.9403	1.59403	56.753
600	8.39265	61.4529	2.4242	57.4138
700	8.52822	62.7569	3.27063	58.0863
800	8.62564	63.9019	4.12858	58.7434
900	8.69775	64.9217	4.99492	59.3745
1000	8.75272	65.8405	5.86756	59.9762
1100	8.79575	66.6762	6.74507	60.5482
1200	8.83027	67.4424	7.62643	61.0916
1300	8.85858	68.1498	8.51091	61.6081
1400	8.8823	68.8065	9.39799	62.0995
1500	8.90256	69.4194	10.2873	62.5677
1600	8.92021	69.994	11.1784	63.0145
1700	8.93591	70.5346	12.0712	63.4415
1800	8.9502	71.0451	12.9656	63.8503
1900	8.96354	71.5288	13.8612	64.2423
2000	8.97635	71.9882	14.7582	64.6187
2100	8.989	72.4259	15.6565	64.9806
2200	9.00182	72.8437	16.556	65.329
2300	9.01516	73.2435	17.4569	65.665
2400	9.0293	73.6268	18.3591	65.9893
2500	9.04449	73.995	19.2628	66.3027
2600	9.06099	74.3494	20.168	66.6059
2700	9.07897	74.6911	21.075	66.8996
2800	9.09862	75.021	21.9839	67.1843
2900	9.12004	75.34	22.8948	67.4606
3000	9.14333	75.6489	23.808	67.729

$$H_{298}^o - H_o^o = 2.11393 \text{ kcal/mol}$$

Molecular Weight: 104.906

$$\omega_e = 862.0 \text{ cm}^{-1} \quad \omega_e x_e = 2.86 \text{ cm}^{-1} \quad \alpha = 0.0016 \text{ cm}^{-1} \quad \beta_e = 0.3892 \text{ cm}^{-1}$$

Electronic States

$\epsilon_i \text{ (cm}^{-1}\text{)}$	g_i
0	2
16315	2
16746.8	2

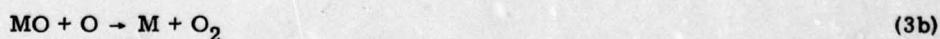
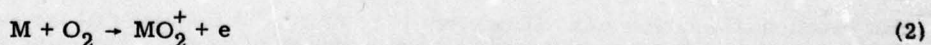
Table 4. Thermochemical Data for the Gaseous Metal Dioxides

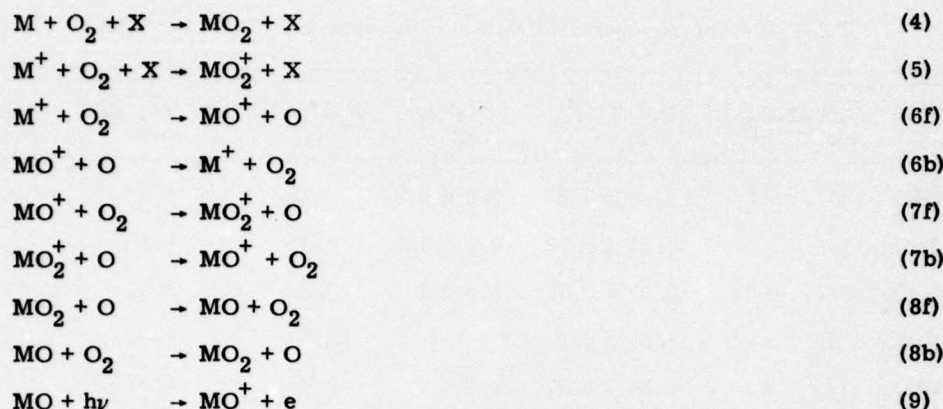
MO ₂	$\Delta H_a(\text{MO}_2)^a$ kcal/mol	$\Delta H_a(\text{MO}_2)^a$ eV	IP(MO ₂) eV	D _O ⁰ (MO-O) ^b eV	D _O ⁰ (MO ⁺ -O) ^c eV	Reference
CeO ₂	344 ± 5	14.92 ± 0.22	9.8 ± 0.5	6.76	1.9	69, 70
FeO ₂	199.0 ± 5	8.64 ± 0.22	9.5 ± 0.5	4.43	3.6	28
GdO ₂	314 ± 17	13.6 ± 0.7	9.5 ± 1	6.3	2.6	69
NdO ₂	318 ± 20	13.8 ± 0.9	---	6.6	---	69
PbO ₂	190 ± 5	8.24 ± 0.22	8.9 ± 1	4.41	4.5	39
SeO ₂	199.6 ± 5	8.65 ± 0.22	---	4.3	---	43
SiO ₂	302 ± 8	13.1 ± 0.35	11.5 ± 0.5	4.82	4.9	45
ThO ₂	366.2 ± 7.2	15.9 ± 0.3	8 ± 1	7.1	≥ 5.1	52
TiO ₂	304.0 ± 2.8	13.18 ± 0.12	9.54 ± 0.1	6.31	3.5	55
UO ₂	352.5 ± 5	15.29 ± 0.22	5.4 ± 0.1	7.43	7.8	57, 14
ZrO ₂	331.3 ± 3.6	14.4 ± 0.3	9.4 ± 0.2	6.5	3.1	64

- a. $\Delta H_a(\text{MO}_2)$ is the heat of atomization and is the energy required for the process: $\text{MO}_2 \rightarrow \text{M} + 2\text{O}$.
- b. $D_O^0(\text{MO}-\text{O})$ was taken to be $\Delta H_a(\text{MO}_2) - D_O^0(\text{MO})$; $D_O^0(\text{MO})$ was taken from Table 1.
- c. $D_O^0(\text{MO}^+-\text{O})$ is the energy required for the process $\text{MO}_2^+ \rightarrow \text{MO}^+ + \text{O}$. $D_O^0(\text{MO}^+-\text{O}) = D_O^0(\text{MO}-\text{O}) + \text{IP}(\text{MO}) - \text{IP}(\text{MO}_2)$.

3. KINETIC DATA

The thermochemical data presented above have interesting implications regarding atmospheric reactions of metallic species. Before these are discussed, however, a few general reactions will be written and reference will be made to them in the discussion:





Tables 5 and 6 present a summary of the available kinetic data in the form of cross section data (Table 5) or in the form of rate constants (Table 6). As can be seen, the information available is rather sparse and many more rate constants need to be measured. Where there is data available on the forward (or back) reaction rate constant, the rate constant for the reverse reaction was calculated from the equilibrium constant ($k_{eq} \equiv k_{nf}/k_{nb}$, where the subscripts f and b denote forward and back reaction, respectively). The equilibrium constant was calculated from thermodynamic data and free energy functions. In some cases, for example, the metal oxide ions, it was necessary to calculate these functions.

Table 5. Thermal Energy Reaction Cross Sections*

M	σ_1	σ_2	σ_{6f}	M	σ_1	σ_2	σ_{6f}
Al			**	Sm	1.7		
Ce	1	0.003		Th	10.0	0.15	
Gd	8.4			Ti	45.0		
La	51.0	0.17		U	16.0	0.17	
Nd	27.0			Y	3		
Pr	20	0.004		Zr	13		

* Cross sections are in units of 10^{-16} cm^2 . Unless otherwise noted, this data was taken from a summary given in Reference 71.

** The reaction is endothermic. Data given in reference 72 indicate that the reaction cross section has a maximum at a kinetic energy of $\approx 8 \text{ eV}$. The value at this maximum is about $5 \times 10^{-17} \text{ cm}^2$.

Table 6. Thermal ($T \approx 300$ K) Rate Constants for Reactions Forming or Destroying Metal Oxides^a

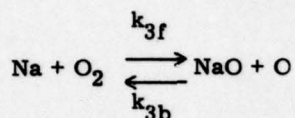
M	k_1^b	k_2^b	k_{3f}^c	k_{3b}^c	k_4^d	k_5^d	k_{6f}^c	k_{6b}^c	k_{7f}^c	k_{7b}^c	k_{8f}^c	k_{8b}^c
Al	0.34 ± 0.22^e											
Ba												
Ca						$\sim 6.6^h$						
Fe			$[10^{-16}]^f$	$[0.33]^g$		$\sim 1.0^h$						
K						$< 0.2^h$						
Mg						$\sim 2.5^h$	$[5 \times 10^{-32}]^i$	$\sim 1.0^h$				
Na						$< 0.2^h$						
Pb												
Si							$[8 \times 10^{-6}]^j$	$\sim 2.0^m$				
Sr												
Th							6 ± 1^k					
Ti							5 ± 1^k	$[10^{-31}]^n$				
U							$8.5_{-4}^{+1} \}^l$		20.3 ± 4.4^o			

- a. k_{nf} refers to rate for forward reaction and k_{nb} refers to rate for back reaction.
b. See Table 5 for cross section data. A rough estimate of k may be obtained from $k = \sigma \cdot v$, where v is the velocity.
c. In units of 10^{-10} cm³/molecule-sec.
d. In units of 10^{-30} cm⁶/molecule²-sec.
e. Reference 73.
f. k_{eq} was calculated at $T = 300$ K from $\Delta H = -RT \ln k_{eq} - T \Delta S$. Since k_{3f} was measured in reference 74, k_{3b} was calculated from k_{eq} .
g. k_{3f} was measured at $T = 1600$ K (reference 74). The functional dependence of k_{3f} on T was assumed to be $k(T) = A e^{-(\Delta E/RT)}$, where A is the frequency factor and ΔE is the activation energy. ΔE is assumed to be equal to ΔH ($= 21.2$ kcal/mol), which leads to $A = 2.7 \times 10^{-10}$. k at 300 K was calculated from this.
h. Reference 75.
i. k_{eq} ($= k_{6f}/k_{6b}$) was calculated at 300 K. k_{6b} was taken from reference 75.
j. k_{eq} ($= k_{6f}/k_{6b}$) was calculated at 300 K. k_{6b} was taken from reference 76.
k. Reference 77.
l. Reference 78.
m. Reference 75.
n. k_{eq} ($= k_{6f}/k_{6b}$) was calculated at 300 K. k_{6f} was taken from reference 77.
o. Reference 79.

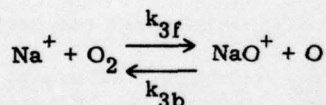
4. DISCUSSION

In light of the thermodynamic and kinetic data presented above, some atmospheric applications can be considered. For example, a recent mass spectrometric study⁸⁰ of positive ion composition at altitudes ranging between 68.5 and 152 km, ions at $m/e = 39$ and 43 were observed and these were attributed to NaO^+ and AlO^+ , respectively. In addition, SiO_2^+ was suggested as an atmospheric species. An

examination of Table 1 shows that there is not an easy way to form NaO^+ , since reaction (1) for Na is endothermic by 4.8 eV. The sequence of reactions (3f) and (9) also seems unlikely since reaction (3f) is endothermic by 2.5 eV. One possibility is the formation of NaO by reaction of Na with O_3 , that is, $\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2$, followed by reaction (9). However, both for NaO and NaO^+ , one would expect these species to be removed very quickly via reactions (3b) and (6b), respectively. To illustrate this point, data from the JANAF thermochemical tables²² were used to calculate the equilibrium constant, k_{eq} , for reactions 3:



at $T = 200$ K, which is approximately the temperature at an altitude of about 95 km.⁸¹ For this reaction $\Delta H_r = 57.7$ kcal/mol (2.5 eV), which is $D_0^{\text{O}}(\text{O}_2) - D_0^{\text{O}}(\text{NaO})$. From the JANAF data, an equilibrium constant ($k_{\text{eq}} = k_{3f}/k_{3b}$) of $\sim 4 \times 10^{-62}$ is calculated. At 95 km $[\text{O}]/[\text{O}_2] \approx 0.035$ so that $[\text{NaO}]/[\text{Na}] \approx 10^{-60}$. Clearly, very little NaO will be observed under these conditions. The analogous reactions with NaO^+ , that is



are expected to be equally one-sided towards Na^+ . There are no spectroscopic studies of NaO^+ so that its thermodynamic functions cannot be calculated accurately. However, NaO^+ is isoelectronic with NeO so that it may be possible to use the latter as a model; indeed, recent theoretical calculations⁸³ indicate that NeO has an unbound ground state, which is similar to the thermochemical data for NaO^+ , as shown in Table 1. The calculated functions may have large uncertainties since the integral method of calculating the entropy may not be very accurate for such a shallow potential well; in the absence of vibrational constants, this is the only method possible, since it is not possible to sum up the individual vibrational levels. Table 7 shows the calculated thermodynamic functions for NaO^+ . Using these functions and those of Na^+ , O, and O_2 given in the JANAF tables, k_{eq} is calculated to be $\approx 10^{-120}$! This calculation suggests that perhaps the peak at $m/e = 39$ is not due to NaO^+ . Of course, it may be that thermodynamic equilibrium is not maintained in the upper atmosphere, but that seems unlikely, since even if reaction (3b) did not have a chance to take place, one would expect NaO^+ to decompose quickly in view of its small dissociation energy.

Table 7. Thermodynamic Functions for Gaseous Sodium Monoxide Ion (NaO⁺)

T (K)	C ^o (E. U.)	S ^o (E. U.)	H _T ^o - H ₂₉₈ ^o (kcal/mol)	-(G _T ^o - H ₂₉₈ ^o)/T (E. U.)
100	7.09741	47.2648	-1.54686	61.7333
200	7.87095	52.4225	-1.798167	55.4133
300	8.34396	55.7149	.0154309	54.6634
400	8.57489	58.1507	.86267	54.994
500	8.69941	60.0787	1.72694	55.6248
600	8.7802	61.6723	2.60113	56.3371
700	8.84825	63.031	3.48257	57.0558
800	8.91884	64.217	4.37087	57.7534
900	8.99759	65.272	5.26662	58.4202
1000	9.08428	66.2244	6.17065	59.0537
1100	9.17585	67.0945	7.08364	59.6548
1200	9.2683	67.8969	8.00585	60.2253
1300	9.3579	68.6423	8.9372	60.7675
1400	9.44164	69.3389	9.87724	61.2837
1500	9.51744	69.9929	10.8253	61.7761
1600	9.58406	70.6094	11.7804	62.2466
1700	9.64099	71.1921	12.7418	62.697
1800	9.68825	71.7446	13.7083	63.1289
1900	9.72624	72.2695	14.6791	63.5436
2000	9.75562	72.7692	15.6533	63.9425
2100	9.77719	73.2457	16.63	64.3266
2200	9.7918	73.7009	17.6085	64.697
2300	9.80032	74.1363	18.5881	65.0545
2400	9.80358	74.5535	19.5684	65.4
2500	9.80236	74.9537	20.5487	65.7342
2600	9.79736	75.3381	21.5287	66.0578
2700	9.78924	75.7077	22.508	66.3714
2800	9.77855	76.0635	23.4865	66.6755
2900	9.76579	76.4055	24.4637	66.9707
3000	9.75138	76.7373	25.4396	67.2574

$$H_{298}^o - H_o^o = 2.244 \text{ kcal/mol}$$

Molecular Weight: 38.99

$$\omega_e = 440 \text{ cm}^{-1}$$

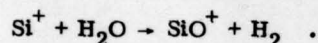
$$I = 3.29 \times 10^{-39} \text{ g-cm}^2$$

Electronic States

$\epsilon_i \text{ (cm}^{-1}\text{)}$	g_i
0	3
4000	3

Similar calculations can be performed for the other metals. Unfortunately, with the exception of AlO^+ little spectroscopic data is available on the molecular properties of the monoxide ions, so that free energy functions have to be calculated using models. In the case of AlO^+ , data from the JANAF tables were used. For FeO^+ , MgO^+ , SiO^+ , and TiO^+ , the isoelectronic neutral monoxides MnO , NaO , AlO , and ScO were used, respectively, as models. The thermodynamic data thus calculated for these molecular ions are shown in Tables 8-11. With these free energy functions, the ratios $[\text{MO}^+]/[\text{M}^+]$ and $[\text{MO}]/[\text{M}]$ were calculated as described in the case of Na above. The results are shown in Table 12. These calculations indicate that it is unreasonable to expect MO^+ to exist in the E-region; at least, it is unreasonable under the assumed conditions, namely $T = 200 \text{ K}$, $[\text{O}]/[\text{O}_2] = 0.035$, and thermodynamic equilibrium.

The case of SiO^+ is somewhat different from the others in that the SiO^+ and Si^+ have the same altitude profile and have a maximum at about 110 km,⁸⁴ where $[\text{O}]/[\text{O}_2] \approx 1$.⁸² It is estimated that $[\text{Si}^+]/[\text{SiO}^+] \approx 10$,⁸⁵ which means that $k_{\text{eq}} \approx 0.1$. To maintain an equilibrium under these conditions the temperature has to be $\approx 1100 \text{ K}$, which is clearly unreasonable at this altitude. Because SiO^+ has the same altitude profile as Si^+ , a possible explanation is that SiO^+ is formed by a reaction of Si^+ with a contaminant in the detector. One possibility is the reaction



According to the data of Table 1 this reaction is endothermic by $0.3 \pm 0.2 \text{ eV}$, so that with a small draw-in potential, Si^+ can easily react with water outgassing from the surfaces. Unfortunately, there is no kinetic data on this reaction so that it is hard to evaluate its importance.

The results of Table 12 also suggest that perhaps the identification of $m/e = 43$ with AlO^{+80} and $m/e = 72$ with FeO^{+86} may need to be reexamined. Likewise, it is not clear how FeO_2^+ can be formed,⁸⁶ and, even if formed, it is not clear why it would not disappear immediately via reaction (7b). This question has been raised in an earlier study.⁸⁷

In passing it is worth noting that superoxides, such as NaO_2 , KO_2 , and CsO_2 have been postulated as constituents of flames⁸⁸ and it has been suggested that they are formed via reaction (4). The evidence is indirect and it seems unreasonable to expect these oxides to be formed at high temperatures; indeed the only firm identification of these oxides has been at low temperatures in matrix-isolation studies.^{89, 90, 91}

Table 8. Thermodynamic Functions of Gaseous Iron Monoxide Ion (FeO^+)

T (K)	C° (E. U.)	S° (E. U.)	$H_T^{\circ} - H_{298}^{\circ}$ (kcal/mol)	$-(G_T^{\circ} - H_{298}^{\circ})/T$ (E. U.)
100	6.95693	50.809	-1.42217	64.0306
200	7.13679	55.6651	-.720605	58.2681
300	7.56566	58.6377	.013989	57.5911
400	7.94753	60.8692	.790593	57.8927
500	8.21631	62.6735	1.59965	58.4742
600	8.39826	64.1887	2.43096	59.137
700	8.52308	65.4932	3.27741	59.8112
800	8.61099	66.6374	4.13436	60.4694
900	8.67467	67.6555	4.9988	61.1012
1000	8.72202	68.572	5.86875	61.7032
1100	8.75805	69.4051	6.74283	62.2752
1200	8.78606	70.1684	7.62009	62.8183
1300	8.80821	70.8725	8.49985	63.3342
1400	8.82601	71.526	9.38159	63.8248
1500	8.84053	72.1354	10.2649	64.2921
1600	8.85251	72.7064	11.1496	64.7378
1700	8.8625	73.2434	12.0354	65.1637
1800	8.87093	73.7502	12.9221	65.5712
1900	8.8781	74.23	13.8095	65.9618
2000	8.88424	74.6856	14.6976	66.3367
2100	8.88955	75.1191	15.5863	66.6971
2200	8.89416	75.5328	16.4755	67.0439
2300	8.89819	75.9282	17.3652	67.3782
2400	8.90174	76.307	18.2552	67.7007
2500	8.90489	76.6705	19.1455	68.0123
2600	8.90767	77.0198	20.0361	68.3136
2700	8.91016	77.356	20.927	68.6053
2800	8.91239	77.6801	21.8181	68.8879
2900	8.9144	77.9929	22.7095	69.162
3000	8.91621	78.2951	23.601	69.4281

$$H_{298}^{\circ} - H_0^{\circ} = 2.11742 \text{ kcal/mol}$$

Molecular Weight: 71.8464

$$\omega_e = 830 \text{ cm}^{-1}$$

$$I = 9.99 \times 10^{-39} \text{ gm cm}^2$$

Electronic States

$\epsilon_i \text{ (cm}^{-1}\text{)}$	g_i
0	6

Table 9. Thermodynamic Functions of Gaseous Magnesium Monoxide Ion (MgO^+)

T (K)	C^0 (E. U.)	S^0 (E. U.)	$H_T^0 - H_{298}^0$ (kcal/mol)	$-(G_T^0 - H_{298}^0)/T$ (E. U.)
100	6.9636	47.1941	-1.44875	60.6816
200	7.28699	52.0925	-.740234	54.7936
300	7.79256	55.1453	.0144084	54.0973
400	8.15685	57.4408	.813209	54.4078
500	8.38746	59.2877	1.64131	55.0051
600	8.5347	60.8309	2.48794	55.6843
700	8.6322	62.1544	3.34661	56.3735
800	8.69934	63.3117	4.21338	57.0449
900	8.74723	64.3392	5.08584	57.6883
1000	8.78246	65.2628	5.96241	58.3003
1100	8.80905	66.1011	6.84204	58.8811
1200	8.82959	66.8685	7.72402	59.4318
1300	8.84576	67.5759	8.60782	59.9545
1400	8.85871	68.232	9.49306	60.4512
1500	8.86924	68.8435	10.3795	60.9239
1600	8.87791	69.4162	11.2669	61.3744
1700	8.88513	69.9547	12.155	61.8046
1800	8.8912	70.4627	13.0438	62.2161
1900	8.89636	70.9436	13.9332	62.6103
2000	8.90078	71.4	14.8231	62.9884
2100	8.90459	71.8344	15.7134	63.3518
2200	8.9079	72.2487	16.604	63.7014
2300	8.91079	72.6447	17.4949	64.0382
2400	8.91333	73.024	18.3861	64.3631
2500	8.91558	73.3879	19.2776	64.6769
2600	8.91758	73.7377	20.1692	64.9802
2700	8.91936	74.0742	21.0611	65.2738
2800	8.92095	74.3987	21.9531	65.5583
2900	8.92239	74.7117	22.8453	65.834
3000	8.92368	75.0142	23.7376	66.1017

$$H_{298}^0 - H_O^0 = 2.14388 \text{ kcal/mol}$$

$$\text{Molecular Weight} = 40.3114$$

$$\omega_e = 700 \text{ cm}^{-1}$$

$$I = 5.78 \times 10^{-39} \text{ gm cm}^2$$

Electronic States

$\epsilon_i \text{ (cm}^{-1}\text{)}$	g_i
0	4

Table 10. Thermodynamic Functions of Gaseous Silicon Monoxide Ion (SiO^+)

T (K)	C° (E. U.)	S° (E. U.)	$H_T^\circ - H_{298}^\circ$ (kcal/mol)	$-(G_T^\circ - H_{298}^\circ)/T$ (E. U.)
100	6.95531	45.8647	-1.40127	58.8774
200	7.03244	50.6979	-.70361	53.2159
300	7.33908	53.6016	.013571	52.5563
400	7.7	55.7632	.765824	52.8486
500	7.99517	57.5146	1.55126	53.4121
600	8.21544	58.9928	2.36233	54.0555
700	8.38331	60.2723	3.1926	54.7114
800	8.5232	61.401	4.03807	55.3534
900	8.65372	62.4125	4.89694	55.9714
1000	8.78623	63.3311	5.76889	56.5622
1100	8.92576	64.175	6.65442	57.1255
1200	9.07269	64.9579	7.55429	57.6626
1300	9.22458	65.69	8.46913	58.1753
1400	9.37762	66.3793	9.39924	58.6655
1500	9.52765	67.0314	10.3445	59.135
1600	9.67085	67.6509	11.3045	59.5856
1700	9.8041	68.2413	12.2784	60.0187
1800	9.92512	68.8052	13.265	60.4357
1900	10.0324	69.3447	14.263	60.8379
2000	10.1253	69.8617	15.271	61.2262
2100	10.2037	70.3577	16.2875	61.6017
2200	10.2679	70.8339	17.3112	61.9651
2300	10.3188	71.2915	18.3407	62.3173
2400	10.3572	71.7315	19.3746	62.6588
2500	10.3844	72.1549	20.4117	62.9902
2600	10.4015	72.5626	21.4511	63.3121
2700	10.4097	72.9553	22.4917	63.625
2800	10.4101	73.3339	23.5328	63.9293
2900	10.4039	73.6991	24.5735	64.2255
3000	10.392	74.0517	25.6134	64.5138

$$H_{298}^\circ - H_0^\circ = 2.09626 \text{ kcal/mol}$$

Molecular Weight = 48.0854

$$\omega_e = 1000 \text{ cm}^{-1}$$

$$I = 5.18 \times 10^{-39} \text{ gm cm}^2$$

Electronic States

$\epsilon_i \text{ (cm}^{-1}\text{)}$	g_i
0	2
5000	4

Table 11. Thermodynamic Functions of Gaseous Titanium Monoxide Ion (TiO^+)

T (K)	C° (E. U.)	S° (E. U.)	$H_T^\circ - H_{298}^\circ$ (kcal/mol)	$-(G_T^\circ - H_{298}^\circ)/T$ (E. U.)
100	6.95531	47.4069	-1.40127	60.4195
200	7.03244	52.24	-.70361	54.758
300	7.33908	55.1437	.013571	54.0985
400	7.69998	57.3053	.765823	54.3907
500	7.9947	59.0567	1.55124	54.9542
600	8.2119	60.5346	2.36216	55.5976
700	8.36887	61.8129	3.19162	56.2534
800	8.48326	62.9382	4.03452	56.8951
900	8.56808	63.9426	4.88729	57.5122
1000	8.6322	64.8488	5.74744	58.1013
1100	8.68162	65.6739	6.61324	58.6619
1200	8.72037	66.4311	7.48341	59.1949
1300	8.75127	67.1303	8.35705	59.7018
1400	8.77628	67.7798	9.23347	60.1845
1500	8.79685	68.386	10.1122	60.6446
1600	8.81405	68.9543	10.9927	61.0839
1700	8.82871	69.4891	11.8749	61.5039
1800	8.84155	69.9942	12.7584	61.9061
1900	8.85314	70.4725	13.6432	62.2919
2000	8.86399	70.9269	14.529	62.6624
2100	8.87458	71.3596	15.4159	63.0187
2200	8.88533	71.7727	16.3039	63.3618
2300	8.8966	72.1679	17.193	63.6927
2400	8.90874	72.5468	18.0833	64.0121
2500	8.92205	72.9108	18.9748	64.3208
2600	8.93676	73.261	19.8677	64.6195
2700	8.9531	73.5985	20.7622	64.9088
2800	8.97121	73.9245	21.6584	65.1893
2900	8.99122	74.2396	22.5565	65.4615
3000	9.0132	74.5448	23.4567	65.7259

$$H_{298}^\circ - H_0^\circ = 2.09636 \text{ kcal/mol}$$

Molecular Weight = 63.8994

$$\omega_e = 1000 \text{ cm}^{-1}$$

$$I = 6.45 \times 10^{-39} \text{ gm cm}^2$$

Electronic States

$\epsilon_1 (\text{cm}^{-1})$	g_1
0	2
16000	4

Table 12. Calculated Ratios of $[\text{MO}^+]/[\text{M}^+]$ and $[\text{MO}]/[\text{M}]$ at $T = 200 \text{ K}$ and $[\text{O}]/[\text{O}_2] = 0.035$

M	ΔH_r^* kcal/mol	k_{eq} ($\equiv k_{6f}/k_{6b}$)	$[\text{MO}^+]/[\text{M}^+]$	ΔH_r^* kcal/mol	k_{eq} ($\equiv k_{3f}/k_{3b}$)	$[\text{MO}]/[\text{M}]$
Al	78.9	6×10^{-85}	$\sim 10^{-83}$	-3.4	1.7×10^4	$\sim 5 \times 10^5$
Fe	39.9	1.5×10^{-43}	4×10^{-42}	21.2	5×10^{-23}	1.5×10^{-21}
Mg	?	—	—	38	4×10^{-41}	10^{-39}
Na	110.7	10^{-120}	10^{-118}	57.7	4×10^{-62}	10^{-60}
Si	8.3	3.7×10^{-9}	$\sim 10^{-7}$	-72.9	3×10^{79}	10^{81}
Ti	-43.8	6×10^{47}	2×10^{49}	-40.4	4×10^{44}	10^{46}

*Negative ΔH_r indicates exothermic reaction. $1 \text{ eV} / 23.062 \text{ kcal/mol}$.

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